

facial, contamination was encountered along the walls of the Teflon channel through which the metering rod passes. Because this contamination was not eliminated by repeated changes in injector design, the use of three injectors in a series path was adopted. Tailing and other adverse effects due to injection at a point far removed from the column were expected, but have been demonstrated to be nonexistent. The same process stream injected at those points nearest and farthest from the column give chromatograms which may be superimposed.

After its installation in the chemical plant, about

six months were required to work out a satisfactory injector design and to eliminate minor irregularities in the overall operation of the analyzer. Since then, the instrument has performed in a very satisfactory manner and its consistently yielding reliable data. The photograph in Figure 7 indicates the general appearance of the automatic control console of the instrument.

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Driers Based on Tall Oil—A Review¹

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Abstract

The metal soaps of tall oil were introduced as paint driers during World War II. Paint industry experience reveals that these oxidation-polymerization catalysts are generally equivalent in performance to naphthenate driers. Physical properties, manufacturing procedures and application of tallate driers in typical paint systems are reviewed.

Introduction

DRIERS ARE MATERIALS which accelerate the hardening of paints, varnishes and related coatings by catalyzing the polymerization and oxidation of the unsaturated oils or alkyds used as film-forming vehicles.

Drying catalysts used at the present time are derived from active drying metals, like cobalt, manganese and lead, and from auxiliary drying metals, like calcium, zirconium, zinc and others.

In order to function as driers, these metals must be converted to compounds possessing good solubility in paint vehicles and having the "right" chemical configuration. Both requirements are important. Compounds, like tetraethyl lead, in which the metal is linked directly to carbon, do not have any catalytic activity although they have the required solubility characteristics. Compounds, like lead stearate, which have the configuration necessary for catalytic activity, function poorly as driers because of their limited solubility in paint vehicles. The drying metal soaps of naphthenic acid, 2-ethylhexanoic acid and tall oil possess both the solubility characteristics and chemical configuration required for good functionality as driers. These metal soaps are the present day driers of commerce.

It is the purpose of this paper to review the properties, methods of manufacture and applications of the tallate driers, i.e., of the drying metal soaps of tall oil.

Tallate driers were introduced during the early stages of World War II. The curtailment of marine shipping of materials of a non-strategic nature was a severe handicap to the paint industry as naphthenic acid is obtained primarily from Eastern European crude oils and Romanian oils, and therefore was in short supply. The coatings industry's concerted effort to obtain a more readily available, economic drier

acid resulted in the commercial utilization of tall oil in the manufacture of driers.

Tallate driers started with the usual cobalt, manganese and lead soaps. As the drier soaps are generally tacky solids, difficult to handle and to incorporate into paints and varnishes, they are supplied as solutions in volatile hydrocarbon solvents at standardized metal contents. Naphthenate driers are standardized at 6% cobalt, 6% manganese and 24% lead metals. These are referred to as a 6,6,24 line of driers. Because of limitations in technology, the first tallate driers contained only 4% cobalt, 4% manganese and 16% lead metals, i.e., a 4,4,16 line.

Advances in the technology of tall oil refining and drier manufacture now make it possible to produce a 6,6,24 tallate line with properties comparable to those of the naphthenates.

Driers based on tall oil are assuming a greater proportion of the total driers used in the industry every year. Although the total poundage of tallate driers has not increased appreciably over the past ten years, the percentage has increased from approx 13% in 1950 to over 25% in 1962. These percentages are based on the total output of tallate and naphthenate driers. The increasing percentage of tallate driers sold, compared to the total usage of driers, may be attributed mainly to two factors. Advances made in the technology of tall oil refining have upgraded the raw material significantly. Increased knowledge of the processes involved in manufacturing driers from tall oil also has contributed to the expanded usage of this product.

Table I shows the approx production in millions of lb of naphthenate and tallate driers for the years 1950 through 1962 (Production of Synthetic Organic Chemicals, U.S. Tariff Commission). The inordinate in-

TABLE I

Year	Production in mm lb		Percentage of production	
	Tal-lates	Naphthe-nates	Tal-lates	Naphthe-nates
1950.....	5.0	24.0	17.2	82.7
1951.....	11.0	17.0	39.3	60.7
1952.....	5.5	19.0	22.5	77.5
1953.....	5.5	19.0	22.5	77.5
1954.....	5.5	19.0	22.5	77.5
1955.....	5.5	20.0	21.6	78.4
1956.....	5.0	19.0	22.9	77.1
1957.....	5.0	21.0	21.2	78.8
1958.....	6.0	17.0	26.1	73.9
1959.....	7.0	17.0	29.2	70.8
1960.....	5.0	15.0	25.0	75.0
1961.....	7.0	14.0	33.3	66.7
1962.....	8.0	15.0	35.8	64.2

¹ Presented at the AOCS Meeting, New Orleans, 1964.

TABLE II
 Drying Times of Coatings Systems

System	Drying time in hr		% Metal
	Tal-lates	Naphthe-nates	
1. Aluminum paint	2.00	1.80	0.04 Co 0.30 Pb 0.02 Co
2. Conventional linseed oil house paint	5.00	5.00	0.10 Zn 0.06 Co 0.50 Pb 0.07 Co
3. (a) White alkyd gloss	3.25	3.00	0.07 Co 0.50 Pb 0.07 Co
(b) White alkyd gloss	3.25	3.25	0.07 Co 0.50 Pb
4. (a) White alkyd semi-gloss	4.20	5.25	0.07 Co 0.07 Co 0.12 Ca
(b) White alkyd semi-gloss	3.75	4.00	0.54 Pb 0.06 Co
5. Black alkyd enamel	4.00	4.00	0.80 Pb 0.10 Co
6. Blue oleoresinous enamel	7.00	6.80	0.06 Co 0.10 Ca
7. 52-R-13 Alkyd	4.50	4.40	0.08 Co 0.70 Pb
8. Linseed oil emulsion paint	8.00	8.00	0.50 Pb 0.02 Co 0.02 Mn
9. Polyurethane varnish	0.50	0.80	

crease in 1951 in the production of tallate driers was due almost exclusively to the Korean War, where again, naphthenic acid was in short supply. From 1952 to 1962 a slight, but steady, increase in the poundage of tallate driers is evident. On the other hand, the production of naphthenate driers during the same years shows a decline from approx 82% of the driers manufactured in 1950 to only 64% of the driers made in 1962.

Properties of Tallate Driers

The physical properties of tallate driers of importance to the paint manufacturer are color, viscosity, storage stability and solubility in paint vehicles and diluents.

The first tallate driers were dark in color, very viscous at the standard 6,6,24 metal concn, and poorly soluble in paint vehicles. To overcome these defects, the drier solutions were supplied at metal contents of 4,4 and 16%, which corresponded to an average non-volatile or metal soap content of ca. 50%.

After World War II, advances in tall oil refining resulted in tall oil acids of improved color and lower average combining wt. Simultaneously, improvements were made in the processes of manufacturing driers through the use of stabilizers, solubilizers and viscosity modifiers, such as dibutyl tartrate (1), alkyl acid phosphates (2) and others. As a result, tallate driers are today equal in color and solubility characteristics to their naphthenate counterparts. They are supplied at the standard 6,6,24 metal concn, which correspond to an average nonvolatile content of ca. 70% compared to 60% for the naphthenates. Despite this appreciable difference in nonvolatile content, only minor differences in viscosity exist between tallate and naphthenate driers.

Tall oil, unlike naphthenic acid, contains unsaturated acids which, as their metal soaps, tend to oxidize when exposed to air and UV light. This oxidative instability results in the formation of insoluble precipitates when tallate driers are exposed to the atmosphere. However, these problems have been overcome by the use of antioxidants and other stabilizers.

Tallate driers, particularly lead, are more sensitive to moisture than naphthenates. The presence of moisture tends to cause the separation or precipitation of insoluble lead soaps of saturated fatty acids found in

 TABLE III
 Tack-Free Dry Time (Hr) Comparison of Tallates, Naphthenates and 2-Ethylhexoates

System	Tal-late	Naphthe-nate	2-Ethyl-hexoate
Alkyd gloss enamel			
0.07 Co; 0.5 Pb	2.75	3.75	2.75
0.07 Co; 0.12 Ca	2.75	3.80	2.75
0.10 Mn; 0.7 Pb	6.25	7.30	6.25
Alkyd semi-gloss enamel			
0.07 Co; 0.5 Pb	2.75	3.00	2.40
0.07 Co; 0.2 Ca	2.25	2.25	2.25
Commercial alkyd semi-gloss enamel			
0.07 Co	4.50	4.50	4.70
0.07 Co; 0.5 Pb	3.50	3.50	3.70
0.07 Co; 0.5 Pb; 0.05 Ca	3.50	3.50	3.25
0.07 Co; 0.12 Ca	3.50	3.50	3.00
0.10 Mn	7.75	7.75	7.75
0.10 Mn; 0.7 Pb	4.50	4.50	4.50

Films were applied on glass with a 1.5-mil Bird applicator. Drier content is expressed as percentage of metal based on non-volatile vehicle.

tall oil. Again, the use of stabilizers has minimized this sensitivity.

As the result of improvements in physical properties and storage stability, tallate driers now seriously challenge the once dominant position of the naphthenate driers.

Manufacturing Processes

Lead, cobalt and manganese driers may be manufactured from a wide variety of tall oil products. However, it has been found that tall oil fatty acids are especially suitable for the manufacture of lead tallate driers, producing drier solutions that are the most stable in storage and lowest in viscosity. Similarly, distilled tall oil containing 60-70% fatty acids and 23-35% rosin acids is generally preferred for the manufacture of cobalt and manganese tallate driers.

Tallate driers are manufactured by three processes—fusion, double decomposition and direct metal reaction.

The fusion process consists of the reaction of a metal oxide or hydroxide with tall oil. The process is rapid, simple and easy to control. The only by-product is a relatively small amt of water which is readily removed. Further, the oxide or hydroxide usually is the least expensive source of metal. Lead and calcium driers are generally manufactured by the fusion process.

When an inexpensive reactive metal oxide is not available, the double decomposition or precipitation process is employed. The process consists of the reaction of a water-soluble drying metal salt with an aqueous solution of sodium tallate to form the metal soap and sodium salt. As the drier soap is insoluble in the aqueous reaction medium, it precipitates as a tacky solid, occluding much sodium salt. In order to avoid washing the impure solid product, Roon and Gotham (3) carried out the chemical reactions in the presence of a volatile hydrocarbon solvent which extracted the product as soon as it had precipitated.

Despite this improvement, the double decomposition process is used only when no other process is available. One of the chief disadvantages is that at the end of the process the reactor contains ca. one-third product and ca. two-thirds aqueous sodium salt solution which is discarded. Manganese and cobalt tallates are manufactured by this process.

The direct metal reaction is a patented process (4), in which air is blown through a mixture of finely divided metal, tall oil and solvent to form the drier soap.

The advantages of this process are similar to those of the fusion process. No inorganic salts are formed as

impurities to be removed. The only by-product is water. The process is direct, does not require large volumes of materials which must later be discarded, and employs the metal itself, usually an economical raw material. The only disadvantage is that it is not as rapid as the fusion process. Cobalt and iron tallate driers are manufactured by the direct metal reaction process.

Application

In general, tallate and naphthenate driers at the same metal content dry paint with equal efficiency. Slight advantages may be found for each drier line in specific paints, but these differences seldom vary by more than 10% of the total drying time.

Other variables affecting the drying time of a paint or enamel, such as temp, humidity, air circulation and others, may cause a 50% deviation in drying time. A temp variation of 20 degrees (68–88F) has been known to cause wide differences in the drying time of an enamel.

Technical journals are replete with data concerning physical properties of driers and methods of manufacture, but very little has been published in the past ten years comparing the relative efficiency of driers made from different anions.

Available data comparing tallate and naphthenate driers indicate no special problem in converting from one drier system to another. Minor differences in color,

viscosity and non-volatile content of the driers become insignificant when reviewed from the aspect of total effect on finished paint properties. For example the degree of variation of viscosity of one batch of paint to the next is often significantly larger than any variation produced by the change in drier.

Table II shows that tallate driers may be used in a multitude of paint systems ranging from linseed oil house paints to the more modern finishes, such as one-package urethanes. While drying times vary considerably among the coatings tested, very little difference in drying time is noted between paints containing naphthenate and tallate driers.

Comparison of the efficiency of the three major types of driers are shown in Table III. The figures shown represent the average of three determinations run on three separate days. It is evident that the tallate driers are equivalent in drying efficiency to naphthenate and octoate (2-ethylhexoate) driers. The comparisons made in Tables II and III show that the selection of the anion plays a minor role in the overall efficiency of metal driers in the coatings industry.

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The Relationship of the Dimer Content of Rosin Determined by Gas Chromatography to Crystallization Time

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Abstract

The resin acid dimer content of rosin influences the crystallization time, as determined with the Burrell-Castor Gelometer. A gas chromatographic packing prepared by treatment of Chromosorb W with dimethyldichlorosilane and trimethylchlorosilane resolved the methyl esters of rosin dimers into 15 components. A vacuum stripping method for assay of rosin dimer agrees with results obtained by quantitative gas chromatography.

Introduction

METHYL ESTERS of rosin can be analyzed for resin acid composition by gas chromatography upon polyester (1) or nitrile silicone gum rubber (2) packings. The methyl esters of fumaric and maleic adducts of resin acids can be chromatographed upon short columns packed with a 2% liquid phase of silicone gum rubber (3). The methyl esters of resin acid dimers have not been eluted from these columns.

Packings prepared by coating Chromosorb® support with siloxane permitted the elution of methyl esters of resin acids, resin acid adducts and resin acid dimers and consequently their determination. Both dimethyldichlorosilane and hexamethyldisilazane (4,5) have been extensively employed to reduce tailing of samples chromatographed on diatomaceous supports. The analytical results obtained by gas chro-

matography were confirmed by a vacuum stripping method.

One method of reducing or eliminating the tendency of tall oil rosin to crystallize is by increasing its dimer content. Crystallization tendency can be measured by oven, refrigeration and solution techniques. Each of the preceding methods is difficult to quantitate because of the human error in judgment involved in fixing the exact crystallization time. The acetone crystallinity method of Palkin and Smith (6) yields relative crystallization rates in a short time although subject to the judgment error. A method has been devised which uses the Burrell-Castor Gelometer. The Gelometer employs a thermostatted bath with a slowly rotating probe connected to a microswitch and timer. When the sample crystallizes, a sharp increase in viscosity of the mixture stops the probe at a preset torque value. No operator attention is required.

Experimental Procedures and Data

Chromatographic packing was prepared by adding 0.8 ml of dimethyldichlorosilane and 0.2 ml of trimethylchlorosilane to 2 g of 60–80 mesh Chromosorb W. This mixture was held in a closed vial for six weeks at room temp. After reaction, the polysiloxane-coated product was treated briefly with 25 ml of boiling methanol, drained and dried.

The chromatographic column was a 76 cm x 0.318 cm OD (0.05 cm wall) 304 stainless steel tube. This